ACP-2011-700: Impact of the deep convection of isoprene and other reactive trace species on radicals and ozone in the upper troposphere, Apel et al.

We are submitting our revised manuscript for your consideration. We were pleased to receive such a positive response from our reviewers and have addressed each of their comments in detail below. While most of the reviewers' comments were of a minor nature, each reviewer had thoughtful and specific questions, mainly to do with requests for clarification of various points. We are grateful for the feedback and hope the manuscript is now more readable and that some specific arguments are easier to follow.

Thank you for your time and attention. We look forward to your final response

Sincerely,

Eric Apel

Reviewer 1:

1. In the abstract it would be helpful to make a little clearer throughout whether the effects for the enhanced isoprene that are discussed are only for presence of low NOx or general. e.g. "PANs persist because of the cold temperatures of the upper troposphere resulting in a large change in the NOx mixing ratios, compared to the case in which no isoprene is convected, a scenario which is also explored by the model." Is the PAN persistence the case for high and no LNOx? Does this equate with high or low NOx? In order to make it easy to distinguish the two types of events I recommend the authors go over the manuscript again to ensure that it is as easy as possible for readers to follow, which type of event is discussed. In most places this is already obvious, but given the importance of the observations and the analysis, which are a great addition to our understanding of this topic, it might be worth it.

OK – clarified this and made changes in the abstract and elsewhere.

2. Figure 7 and discussion. It is mentioned and discussed that observed and modeled formaldehyde agree well during the event. However, before and after the event this is not the case, with observations showing substantially higher values than model. Can the discussion be expanded? Specifically, what confidence can one have that the good model/measurement agreement is meaningful if there is large disagreement other times. Without discussing this more, it might be hard to be convincing that the agreement is not a coincidence.

Yes, thanks – added the following -

The measurements (blue) compare reasonably well with the model (black) for formaldehyde (panel 2), with only a modest increase predicted by the model during the event and the model showing slightly lower mixing ratios. As the CH_2O backgrounds were stable during event 1, we have the most confidence in the CH_2O measurements during this period compared to the measurements before and after this event where the backgrounds were oscillating somewhat.

3. It would be beneficial to explain more clearly why the model of event 1 (figure 7) predicts large production of MVK+MACR (up to 500 ppt as sum) but not for HCHO. Observations reflect this and I assume that low NOx conditions contributes. Specifically, it would be useful to know the high and low NO yields of MVK, MACR and HCHO (not from secondary production) in the model. In fact the paper could possibly provide a useful observational point on yields under low NOx conditions, which is of substantial interest, and perhaps this could be briefly mentioned.

Interesting and good point. Added the following and began a new paragraph afterward:

The relative amounts of the isoprene oxidation products, MVK, MACR, and CH_2O are better understood by considering the processing of these species: Loss of CH_2O is dominated by photolysis (almost 90%), which is uniform before and during the convection event - giving a lifetime of ≈2 hours for CH_2O throughout. Loss of MVK and MACR is dominated by reaction with OH, which is suppressed within the high isoprene event, thus increasing the lifetime from ≈2 hours outside the isoprene plume to 5-8 hours during the high isoprene event.

4. Figure 6: Please explain more clearly what the 3.5 hours and 1.0 hours mean. The main text of the paper does this, but it is not very clear from the caption.

Changed the caption as follows and also added text in document to help clarify this section – see response to Reviewer 2 regarding this figure/subject:

Fig. 6. LaRC DSS model results following injection of 1 ppbv isoprene and 1.5 ppbv NO_x into the boundary layer and shows the predicted (model) and measurement (red points) results for a number of species if the injection took place at a) 15:00 h local sun time, i.e., 3.5 hours before the event was observed, and b) 17:00 h local sun time, i.e, 1.5 h before the event was observed. For each case, the model was run forward with clear-sky J-values (black trace) and then with J-values decreased by a factor of 2 (blue trace). Blue triangles are box model [OH]. See text for further discussion.

Reviewer 2:

Specific Comments
p27245,L4: (OVOC) should be (OVOCs)

changed

p27246,L8: 15 yr should be 15 yrs (plural)

will try but I think ACP editors like it this way

p27254,L6: this is a personal preference, but I don't like the use of "conspire" in this case – makes it seem like something corrupt or fraudulent is going on during the convective events. Maybe replace it simply with something like "combine".

changed

p27254,L21-23: I would suggest including some sort of letter or number to emphasize the important aspects of the photochemical aging discussion, for example:
"This equation holds when 1) no fresh emissions of A are introduced during the trajectory for which the lifetime is calculated, 2) there are no direct emissions of the daughter reaction product, B, and 3) there are no losses via wet or dry deposition."

changed

p27256,L1-3: Please revise the following – it reads awkward and seems repetitive:
"Also, MVK and MACR have larger deposition velocities than isoprene and, according to a recent paper by Karl et al. (2010), indeed have surprisingly high deposition velocities."

Changed to:

Also, MVK and MACR have significantly higher deposition velocities than isoprene (Karl et al., 2010).

p27257,L5: I would insert "(Fig. 4b)" after "trace": "A closer look at the NOx trace (Fig. 4b) reveals. . ."

OK

p27258,L1: Please revise this sentence and try to make a cleaner transition – reading from the previous paragraph to this one was very abrupt.

We looked at this and think a paragraph break is sufficient and the transition not too abrupt because the general subject matter is related to previous paragraphs in the section but the peroxides were used to gain some insight into the event

p27258,Sect3.3: I'm not sure if this is feasible, but for completeness and sequential continuity, it might be useful/insightful to include a comparable analysis for event 1.

It turns out that this is not feasible because the air-mass age (in event 1) precludes a meaningful analysis with the SS model –

p27258,L23-25: revise to something like:

The approach taken here is to mimic, in a simplified way, this convection event by "injecting" a reasonable estimate of NOx (1500 pptv) and boundary layer isoprene

changed

p27259,L8-10: Regarding the following:
"The results indicate that the convection is more rapid than predicted by the photochemical lifetime and are consistent with an approximate time of one hour but with a fair amount of uncertainty."

It is difficult to delineate between the two cases - maybe also include a difference plot or something that can clarify this point. Also, is this purely qualitative by visual inspection or could you include mixing ratios at the crossing points to further highlight this point. Possibly include a supplementary table as SI or something similar to Fig 7.

Good suggestion – added more discussion to delineate between the two cases and to clarify:

…..Figures 6a and b show the results of this exercise. Figure 6a assumes the 3.5 hour upper limit for the transport time and shows the predicted (model) and measurement (red points) results for a number of species if the "injection" took place at 1500 hours. Figure 6b shows results for "injection" of the boundary layer values at 1700 hours local time, i.e., one hour before the event was observed. Results in black are for clear sky J-values and results in blue are for 0.5x the clear sky J-values. The latter values are similar in magnitude to the J-values observed near the top of the updraft. Figure 6a shows that even under the reduced J-value scenario (blue trace), which is unlikely for the span of 3.5 hours, isoprene would have decayed to lower levels than the spread of the observations (150-600 pptv) indicate (red points show the range of isoprene and other measured parameters when the plume was intercepted). Figure 6b is more representative of the observed data. The observed isoprene values are in the range predicted by the model when using clear sky and 0.5x clear sky J-values. The other observed parameters show consistency with this one-hour scenario suggesting that the lifting of boundary layer air to the UT via convection (Event 2) is more rapid than predicted by photochemical age considerations. Since the chemical and physical environment within the updraft is very complex and changes rapidly (Barth et al., 2007), it is difficult to predict the physical and photochemical parameters that strongly affect the ultimate composition of the outflow. This will be the subject of a paper by Fried et al. (in preparation) which will include this particular event in their analysis.

p27261,L22-29: Regarding the following discussion, 1) offset the axis – can't see the gray trace, 2) re-scale the y-axis for a clear presentation.

"In the absence of isoprene injection (gray trace), the model shows very low mixing ratios of MVK, MACR, and MGLY, since these products result only from isoprene oxidation. The third panel down shows formaldehyde. The pulse of isoprene results in a modest increase of formaldehyde. The gray trace shows that formaldehyde is present in the absence of isoprene because it results from the oxidation of many VOCs. There is a significant impact on the OH radical resulting from scavenging by the high isoprene levels, as shown by the difference between the black and gray traces."

Great suggestion - put in color to make this more clear

p27262,L7-9: Please revise the following:
“Recall from the actual event 1 that when the air mass was intercepted by the DC-8, the ratio had already switched in favor of higher reaction products relative to isoprene indicating an aged air-mass.”

Changed to:

Recall from the actual event 1 that when the air mass was intercepted by the DC-8, the ratio had already switched in favor of higher mixing ratios of reaction products relative to isoprene indicating an aged air-mass.

p27262,L21: replace “reacting” with “oxidized”

changed

p27262,L25-25: please revise the following portion of the sentence to be more concise:

“. . .principally because formaldehyde results from reactions further down the isoprene oxidation sequence.”

Changed to: Similarly, formaldehyde shows a large increase initially, but persists longer than MVK, MACR, and MGLY principally because formaldehyde is formed from subsequent reactions of secondary and tertiary products further down the isoprene oxidation sequence.

p27263: There is an overuse of “result” – please revise accordingly.

Yes – thanks – revised

Figure 3: Can you highlight the events with a color band so the are more pronounced visually?

Yes – thanks – did it